

Catalytic behavior of V_2O_5 in rechargeable Li–O₂ batteries

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Abstract The possibility of using vanadium pentoxide (V_2O_5) as a catalyst in rechargeable lithium–oxygen (Li–O₂) batteries was studied. A V_2O_5 -carbon composite was cast onto Ni foam to form a cathode. Electrochemical cells designed based on the flat cell manufactured by Hohen Corporation were fabricated. The initial discharge capacity was 715 mA h g^{-1} , and the maximum discharge capacity reached $2,260 \text{ mA h g}^{-1}$ during the twelfth cycle. The cell had high capacity retention during cycling (1.24 % during cycles 2–8). V_2O_5 acted as a catalyst as well as an active material, improving the specific capacity and capacity retention of the non-aqueous Li–O₂ cell more effectively than do other materials.

Keywords Lithium–air battery · Lithium–oxygen battery · Vanadium pentoxide · Catalyst

1 Introduction

The rapid proliferation of battery-powered electric vehicles (BEVs) in the market has led to the development of high-energy-density storage devices for various applications. Recently, lithium–oxygen (Li–O₂) batteries have attracted

much attention because of their very high specific capacities. This is because Li, which by itself has a high capacity, is used as an anode, and therefore, the use of an active material as a cathode is not required. Consequently, such batteries have much higher capacities than do currently available Li-ion batteries.

The theoretical specific energy of a Li–O₂ battery is $5,200 \text{ W h kg}^{-1}$ (including oxygen storage). In practice, however, oxygen is not stored in the battery, and therefore, its theoretical specific energy excluding oxygen is $11,140 \text{ W h kg}^{-1}$; this is still much higher than those of all other advanced batteries proposed to date and even much higher than those for fuel cells. Abraham and Jiang reported a Li–air battery with a nonaqueous electrolyte [1]. However, this battery has several drawbacks (such as polarization of the oxygen reduction reaction (ORR), high volatility, easy decomposition of the organic electrolyte, and low solubility of Li oxides in the organic electrolyte) that limit its widespread application [2–4].

Most current studies on Li–O₂ batteries focus on porous electrode materials, electrode structures, and catalysis of cell reactions. Numerous researchers have demonstrated that the performance of Li–O₂ batteries can be drastically improved using effective catalysts so that high discharge voltages and discharge rates can be achieved. Thus, developing novel high-activity catalysts for the ORR is imperative. Carbon-supported MnO_x , α - MnO_2 nanowires, γ - $MnOOH$ (manganite), Fe_2O_3 , Fe_3O_4 , CuO , $CoFe_2O_4$, Co_3O_4 , Pt, and Au have previously been used as such cathode catalysts [5–8].

The main purpose of this study was to determine whether V_2O_5 has the potential for use as a catalyst in Li–O₂ batteries. Vanadium pentoxide (V_2O_5) catalysts have extensive industrial applications. For example, they are used in the methanol-based oxidation and reduction of NO_x emissions. Isolated polymeric VO_4 species have been identified as the

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active sites on the surface of dehydrated supported-vanadium-oxide catalysts [9–14].

2 Experimental

2.1 Preparation of O₂ cathode

Carboxymethyl cellulose (CMC) was dissolved in deionized (DI) water. Ketjenblack® (KB) carbon and vanadium pentoxide (V₂O₅, High Purity Chemistry, Inc., Republic of Korea) were then added to the CMC/DI water mixture and were blended using a pestle and mortar. SEM image of V₂O₅ raw material is shown in Fig. 1. It shows the particle size of V₂O₅ raw material is approximately 75 μm. The molar ratio of carbon to catalysts was adjusted to 9:1. The binder accounted for 20 wt% of the total electrode. O₂ cathodes were prepared by casting this DI water/CMC/KB/V₂O₅ slurry onto Ni foam (54–58 cells per inch, cell size: 0.45 mm). The O₂ cathodes were then dried under vacuum at 120 °C for 3 h. Figure 2a shows the high-porosity bare Ni foam chosen as the current collector to provide an open framework that enables rapid oxygen transfer. Figure 2b shows the energy-dispersive X-ray spectroscopy (EDX) image of the V₂O₅-carbon composite cast onto the Ni foam.

2.2 Cell assembly and electrochemical measurements

Electrochemical cells were designed on the basis of HS Flat Cell manufactured by Hohsen Corporation, Japan. A schematic illustration of the fabricated Li–O₂ electrochemical cell based on the HS Flat Cell design is shown in Fig. 3. The cells were assembled in an argon-filled glove

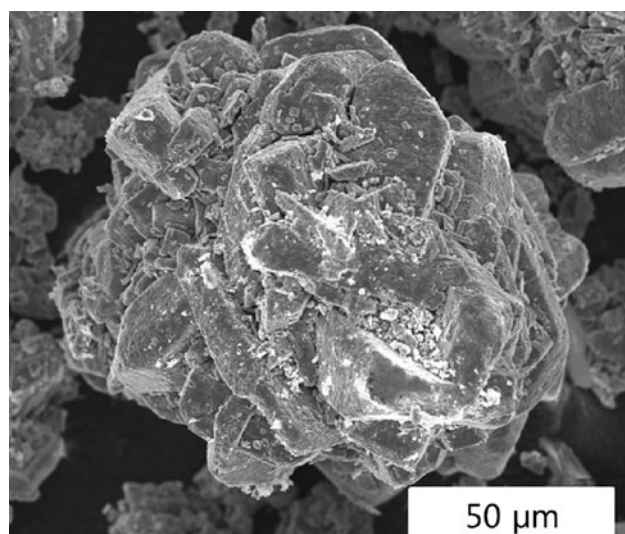


Fig. 1 SEM image of V₂O₅ raw material

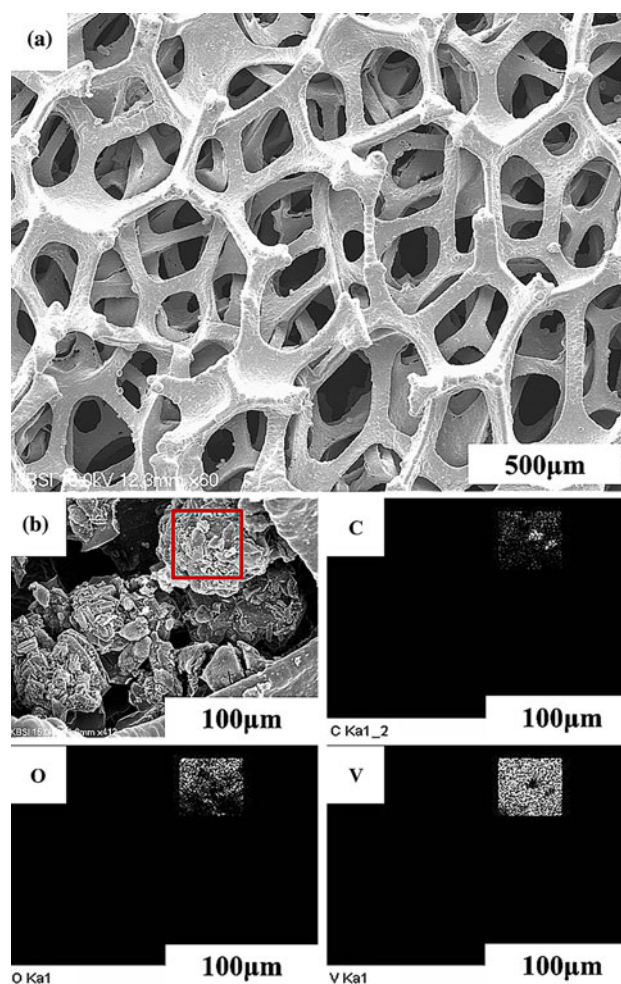


Fig. 2 a SEM image of initial Ni foam and b EDX image of O₂ cathode. Carbon composite cast onto the Ni foam

box. Each cell contained a Li metal anode; a glass micro-fiber filter paper (Whatman® GF/C) impregnated with an electrolyte, 1 M LiPF₆ in PC (Soulbrain, Inc., Republic of Korea); and a porous air cathode. The cells were gas-tight except for the Ni foam window through which the porous cathodes were exposed to the O₂ atmosphere. Experiments were performed in O₂ at 1 atm.

Electrochemical tests were performed by galvanostatically charging/discharging the cells over the range 2–4.5 V at a constant current density of 70 mA g^{−1}. A WBCS 3000 instrument (Wanatech, Inc., Republic of Korea) was used for performing the tests. The cathode morphology was observed using scanning electron microscopy (SEM, Hitachi S-4700, Japan) before cycling.

3 Results and discussion

Figure 4 shows the discharge capacities in cycles 1–15 for the Li–O₂ cell with the V₂O₅ catalyst. The first cycle

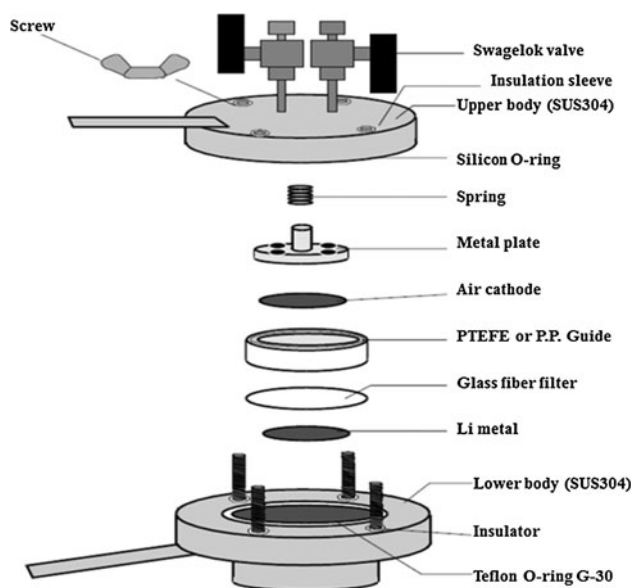


Fig. 3 Schematic of Li–O₂ cell based on HS Flat Cell design

discharge capacity was 715 mA h g^{-1} . The discharge capacity increased to $1,657 \text{ mA h g}^{-1}$ during the second cycle, decreased slightly until the ninth cycle, and increased again to $2,260 \text{ mA h g}^{-1}$ by the twelfth cycle. Thereafter, it continuously decreased. Although V₂O₅ supports Li intercalation to some extent [16], such intercalation does not explain the high capacities shown in Fig. 4.

Table 1 shows their double contribution (active material and catalyst) to capacity. Capacities in some cycles are calculated by V₂O₅ loading and carbon loading. Li–V₂O₅ cell commonly has more than 200 mA h g^{-1} in the initial 20 cycles charge/discharge [17]. These results suggest that

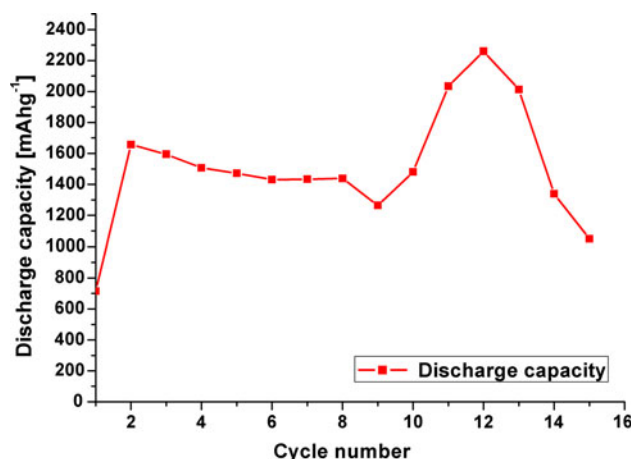


Fig. 4 Variation in discharge capacity over 15 cycles for Li–O₂ cell with V₂O₅ catalyst. Capacities are expressed per gram of carbon in the electrode. Carbon loading was 3.6 mg and V₂O₅ loading was 6 mg . Current density was 70 mA g^{-1}

V₂O₅ can be an effective catalyst for application in Li–O₂ cells. Furthermore, as shown in Fig. 2b, although the V₂O₅–carbon composite could not be cast uniformly onto the Ni foam, higher cell capacity could be achieved if uniform casting was possible.

There are three possible reasons for the capacity reduction after the twelfth cycle: (i) lack of electrical contact because of the separation of the V₂O₅–carbon composite from the Ni foam, (ii) pore blockage in the Ni foam due to the formation of discharge product [15], and (iii) electrolyte depletion [2–4]. Observations made after dismantling the cell indicate that the electrolyte depletion was the dominant factor in the capacity reduction.

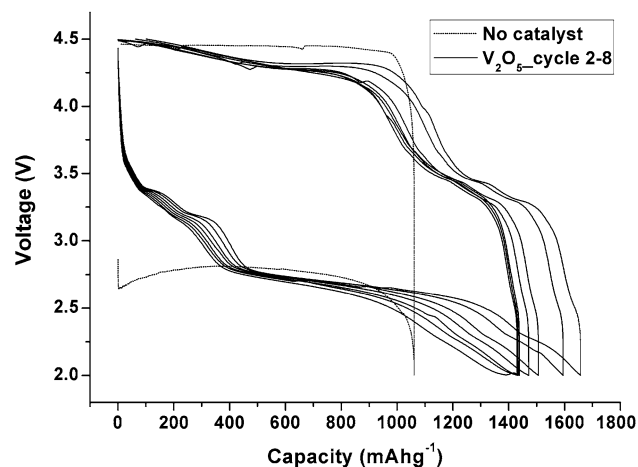
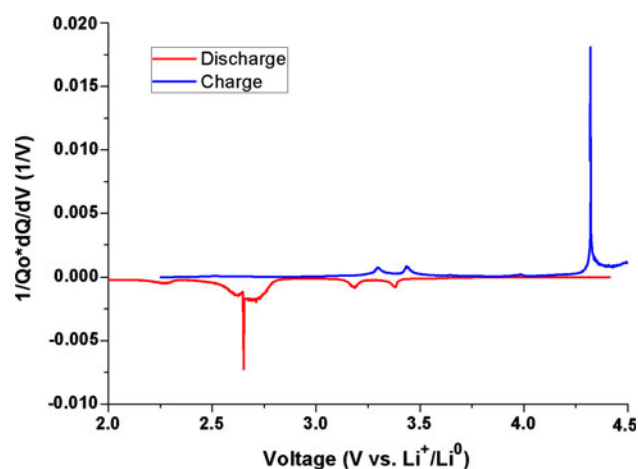
The aforementioned discharge capacities are comparable with those of bulk α -MnO₂, the most commonly used catalyst in Li–O₂ cells [6]. Further, our Li–O₂ cell had high capacity retention during cycling (1.24 % during cycles 2–8). The initial discharge capacity for a porous electrode containing bulk α -MnO₂ as the catalyst was $1,500 \text{ mA h g}^{-1}$, which decreases steadily to 600 mA h g^{-1} in the tenth cycle for a current density of 70 mA g^{-1} . This result suggests that V₂O₅ has catalytic activity comparable to that of bulk α -MnO₂.

Figure 5 shows the cell potentials for a Li–O₂ cell without a catalyst and for one with a V₂O₅ catalyst. The potential for the cell without the catalyst had a charging plateau around 4.5 V. The first cycle discharge capacity was $1,050 \text{ mA h g}^{-1}$. During cycling, the potential for the cell with the V₂O₅ catalyst had three charging plateaus around 3.3, 3.45, and 4.3 V and three discharging plateaus around 2.6, 3.2, and 3.4 V. The clear voltage plateaus around 2.6 and 4.3 V were consistent with the results reported for other Li–O₂ cells with different catalysts, which showed discharge and charge voltages around 2.6 and 4.3 V, respectively [4–7]. These results indicate that the reaction of Li⁺ ions with O₂ was catalyzed by V₂O₅. The cell potential exhibited four clear voltage plateaus between 3.2 and 3.4 V, demonstrating the insertion and extraction of Li⁺ ions in V₂O₅ and showing that V₂O₅ could also act as an active material [16, 17].

Charging and discharging voltages were measured in the range 2–4.5 V for the Li–O₂ cell with the V₂O₅ catalyst and for a conventional Li⁺/Li⁰ cell, and the behavior of the Li–O₂ cell with the V₂O₅ catalyst is clearly depicted in the dQ/dV curve (Fig. 6). The charging potential peaks around 3.3, 3.45, and 4.3 V and discharging potential peaks around 2.6, 3.2, and 3.4 V in the curve clearly indicate that V₂O₅ acted both as a catalyst and as an active material. The peaks between 3.2 and 3.4 V indicate that Li⁺ ions were inserted into and extracted from V₂O₅; thus, V₂O₅ acted as an active material in this voltage range. The two large peaks at 2.6 and 4.3 V are due to the reaction of Li⁺ ions with O₂, indicating that on the whole, V₂O₅ acts as a catalyst by lowering the charging potential of the cell.

Table 1 Discharge capacities calculated by V_2O_5 and carbon loading in second, third, twelfth cycle

| | Second cycle | Third cycle | Twelfth cycle |
|--|--------------|-------------|---------------|
| Discharge capacity per V_2O_5 loading (mA h g^{-1}) | 994 | 956 | 1,356 |
| Discharge capacity per carbon loading (mA h g^{-1}) | 1,657 | 1,594 | 2,260 |

**Fig. 5** Change in voltage profile for Li-O_2 cell without catalyst (KB:CMC (8:2 wt%), carbon loading was 5.2 mg, at a current density of 70 mA g^{-1} and for cell with a V_2O_5 catalyst (KB: V_2O_5 (9:1 mol%) and CMC (8:2 wt%)), at a current density of 70 mA g^{-1} . Capacities are expressed per gram of carbon in the electrode**Fig. 6** dQ/dV curve for second cycle for Li-O_2 cell with V_2O_5 catalyst

4 Conclusions

The hybrid (active and catalytic) behavior of V_2O_5 was explored by studying the ability of the catalyst to enhance

the electrochemical properties of the O_2 electrode in a nonaqueous Li-O_2 cell. The initial discharge capacity was 715 mA h g^{-1} . The discharge capacity reached a maximum of $2,260 \text{ mA h g}^{-1}$ during the twelfth cycle and decreased continuously thereafter. The cell had high capacity retention during cycling (1.24 % during cycles 2–8).

The charging potential peaks around 3.3, 3.45, and 4.3 V and discharging potential peaks around 2.6, 3.2, and 3.4 V clearly indicate the catalytic and active properties of V_2O_5 . The charging potential of 4.3 V indicates that V_2O_5 acted as a catalyst in the Li-O_2 cell.

Further research is required to confirm the present findings and to elucidate the cell reaction mechanism and the nature of the charge/discharge reaction products. These results could be used to reduce the catalyst loading, to ensure uniform casting of the catalyst-carbon composite onto Ni foam, and to minimize total electrode mass, possibly by reducing the V_2O_5 particle size, changing the catalyst morphology, or using a catalyst support such as SiO_2 or Al_2O_3 [18, 19].

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References

1. Abraham KM, Jiang Z (1996) *J Electrochem Soc* 143:1
2. Girishkumar G, McCloskey B, Luntz AC, Swanson S, Wilcke W (2010) *J Phys Chem Lett* 1:2193
3. Kraytsberg A, Eli YE (2011) *J Power Sources* 196:886
4. Padbury R, Zhang X (2011) *J Power Sources* 196:4436
5. Debart A, Bao JL, Armstrong G, Bruce PG (2007) *J Power Sources* 174:1177
6. Debart A, Bao JL, Armstrong G, Bruce PG (2008) *Angew Chem Int Ed* 47:4521
7. Lu YC, Xu Z, Gasteiger HA, Chen S, Schifferli KH, Yang SH (2010) *J Am Chem Soc* 132:12170
8. Cheng H, Scott K (2010) *J Power Sources* 195:1370
9. Miller JM, Lakshmi LJ (2000) *Appl Catal A Gen* 190:197
10. Khaliullin RZ, Bell AT (2002) *J Phys Chem B* 106:7832
11. Irueta S, Cornaglia LM, Miro I, Lombardo EA (1995) *J Catal* 156:167
12. Bond GC, Tahir SF (1991) *Appl Catal* 71:1
13. Bronkema JL, Bell AT (2007) *J Phys Chem C* 111:420
14. Kim T, Wachs IE (2008) *J Catal* 255:197
15. Freunberger SA, Chen Y, Peng Z, Griffin JM, Hardwick LJ, Bardé F, Novák P, Bruce PG (2011) *J Am Chem Soc* 133:8040–8047
16. Braithwaite JS, Catlow CRA, Gale JD, Harding JH (1999) *Chem Mater* 11:1990
17. Zhao H et al (2012) *J Appl Electrochem* 42:139–144
18. Boyano A, Moliner R (2009) *Chem Eng J* 149:173
19. Reddy EP, Varma RS (2004) *J Catal* 221:93